

IV.B.5k Main Group Element and Organic Chemistry for Hydrogen Storage and Activation

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Objectives

- Develop new chemistries to enable DOE to meet the technical objective: "By 2010, develop and verify on-board hydrogen storage systems achieving 2 kWh/kg (6 wt%), 1.5 kWh/L, and \$4/kWh.; by 2015, 3 kWh/kg (9 wt%), 2.7 kWh/L, and \$2/kWh" by using chemical hydrogen storage systems.
- Focus on organic and main group compounds to enable new chemistries which may be able to perform better for release and regeneration by improving the energy balance and to provide longer term alternatives.
- Develop and implement imidazolium (carbene)-based H₂ activation chemistry.
- Develop and implement systems based on main group elements (examples: nitrogen and phosphorus).
- Develop and implement cyanocarbon systems for H₂ storage.
- Provide computational chemistry support (prediction of thermodynamics, kinetics, spectroscopic properties, mechanisms, etc.) to the experimental efforts of the DOE Chemical Hydrogen Storage Center of Excellence (CHSCoE)

to reduce the time to design new materials and develop materials that meet the 2010 and 2015 DOE objectives. Focus on new materials, hydrogen release mechanisms and regeneration processes.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (J) Thermal Management
- (R) Regeneration Processes

Technical Targets

Storage Parameter: DOE 2010 System Targets	Carbene	Cyanocarbon	Phosphacarbons*
Material Gravimetric Capacity: 6 wt%	Current: 2% Ultimate: 7.2%	Current: <1% Ultimate**: 7.2%	Current: <1% Ultimate: 5% with P 7.2% by substituting N for P
Material Volumetric Capacity: 0.045 kg/L	Current: 0.045 Ultimate: 0.098	Current: 0.045 Ultimate: 0.092	Ultimate(P): 0.10 Ultimate(N): 0.092
Dehydrogenation Rate: 0.02g/s-kW	In progress	Oxidation step diffusion limited	Model Study
Storage Efficiency CHSCoE Goal: 50% Near Thermoneutral	Exothermic: -5 kcal/mol Ultimate: Thermoneutral	Endothermic: 5 kcal/mol Ultimate: Thermoneutral	Model Study

* Continue only as a model system to understand release and regeneration

** Ultimate for CN polymer is C₂N₂H₆ = 10.3%

Accomplishments

- Developed first tetracyanoethylene (TCNE) oligomerization procedure for making cyanocarbons for H₂ storage with potential of 10 wt%.
- Continued work on 4-member ring diradicals with P substituents shows H₂ addition and release. Serves as first model for H₂ release from C at room temperature.
- Initial studies demonstrate catalyst photoactivation for H₂ addition to cyanocarbons and carbenes. Potential for widespread applicability.
- Demonstrated weight reduction by oligomerization of carbenes. Demonstrated oxidized and reduced (H₂ on and off) carbenes. Develop mixed carbene/TCNE synthesis to make oligomers.
- First demonstration of **non-metal catalysis** using organic compounds which are photoactivated for release of H₂.
- First set of accurate thermodynamics for B_xN_xH_y compounds up to x = 3 and y = 14 for release and regeneration of ammonia borane (AB) (with Pacific Northwest National Laboratory [PNNL]).
- Accurate bond energies for AB (ammonia borane = BH₃NH₃) and derived systems for release and regeneration (CHSCoE).
- H₂ release processes from AB (BH₃ as a Lewis acid catalyst) (Los Alamos National Laboratory [LANL] and CHSCoE).
- H₂ release processes studied via cationic chain polymerization mechanism (with LANL).
- First reliable thermodynamic properties of B₃H₇NH₃ and decomposition mechanism (University of Pennsylvania [Penn]).
- Study mechanism of H₂ release from AB dimer (BH₃NH₃)₂ and from zwitterionic isomer [NH₃BH₂NH₃⁺][BH₄⁻] – importance of seeding. (PNNL).
- Methyl substituent effects on energetics of borane amine compounds for release and regeneration (mixed solvents) (LANL, PNNL, University of Washington [UW], Penn, Northern Arizona University).
- Extensive studies of energetics for H₂ AB regeneration mechanisms (LANL, PNNL, Penn, University of California, Davis [UC-Davis], UW).
- Energetics for novel chemical H₂ storage systems: carbenes, cyanocarbons, P-based diradicals.



Introduction

The focus of the work is the development of new chemistries to enable DOE to meet the technical

objective: “By 2010, develop and verify on-board hydrogen storage systems achieving 2 kWh/kg (6 wt%), 1.5 kWh/L (0.045 kg H₂/L), and \$4/kWh.; by 2015, 3 kWh/kg (9 wt%), 2.7 kWh/L (0.081 kg H₂/L), and \$2/kWh” by using chemical hydrogen storage systems. We are developing and implementing imidazolium-based H₂ activation chemistry; developing and implementing chemical systems based on polyhydrides of main group elements, e.g., phosphorous; developing and implementing cyanocarbon systems for H₂ storage; developing new non-metal catalysts that can be photoactivated for the release of H₂; and providing computational chemistry support (thermodynamics, kinetics, properties prediction) to the experimental efforts of the DOE CHSCoE to reduce the time to design new materials and develop materials that meet the 2010 and 2015 DOE objectives.

Approach

To achieve the goals described in the Introduction, we are **developing and identifying new concepts** to increase capacity and minimize weight (example: use storage medium for structural benefits); developing new concepts to improve energy balance which is especially relevant for ease of H₂ release and regeneration of the chemical H₂ storage system; developing new approaches to release hydrogen from dihydroimidazoles, based on new chemistry and our world leadership in stable carbene chemistry; and demonstrating proof-of-concepts and key reactions. A key issue is to minimize weight by eliminating substituents or changing them into components that can store H₂ while maintaining kinetic and thermodynamic properties; **developing** new non-metal catalysts that can be photoactivated for the release of H₂; using highly accurate first principles computational chemistry approaches on advanced computer architectures to predict the electronic structure of molecules to obtain thermodynamic and kinetic information in support of the design of hydrogen storage materials and of catalysts to effect easy release and addition of H₂ (regeneration); and developing computational thermodynamic and kinetic approaches for chemical H₂ storage based on exploiting ΔH and ΔG coupled with Le Chatelier's principle to manage H₂ addition and release in chemical compounds. For the experimental effort, there are close interactions with the partners (LANL and UC-Davis). The computational effort supports the entire CHSCoE with special interactions with LANL, PNNL, UW, Penn, UC-Davis, and the University of California, Los Angeles.

Results

Substantial progress has been made this year in terms of the experimental and computational efforts. Experimental advances include: (1) **development** of the first TCNE oligomerization procedure for making

cyanocarbons for H₂ storage with potential of 10 weight %. This is the first time that this has been accomplished even though many man years of research at DuPont were spent on this. This chemistry is directly linked to the carbene/imidazolium chemistry that we have been pursuing and we have been able to demonstrate that the two chemistries will lead to the same storage compositions. The synthesis route for carbene oligomerization is shown in Figure 1 and the

cyanocarbon/carbene condensation approach in Figure 2 together with its x-ray structure; and (2) development of new non-metal catalysts that can be photoactivated for the fixation of H₂ as shown in Figure 3. This is based on our discovery that a stable phosphorus-based bi-radical would chemically add (fix) hydrogen without the need for a transition metal catalyst. We have been able to reduce dyes like methylene blue with dihydrogen in the presence of light. This added hydrogen can be

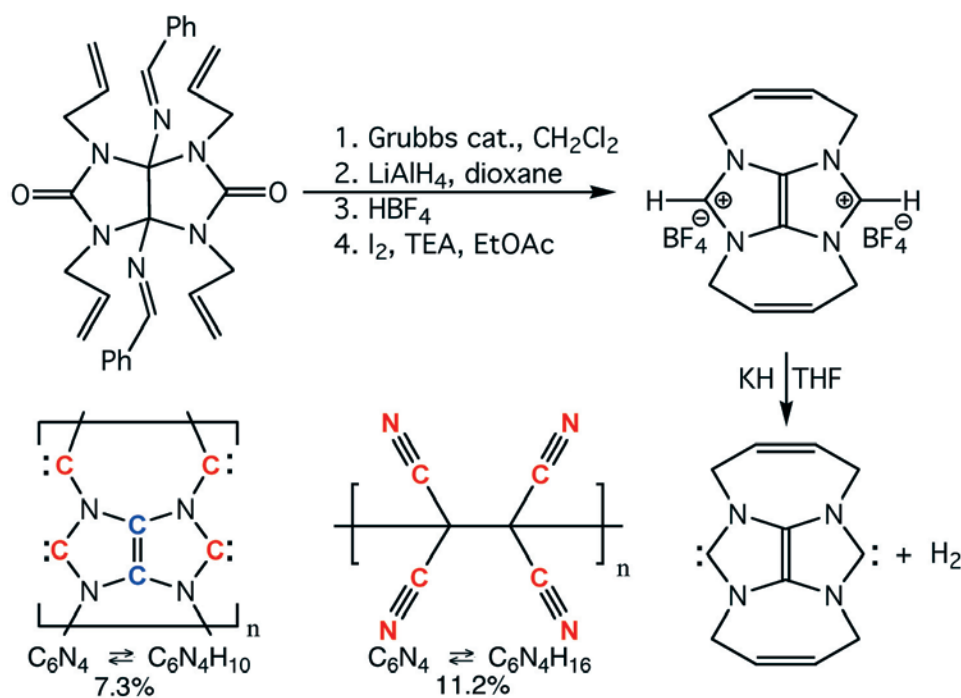


FIGURE 1. Synthetic Approach for the Polymerization of Carbenes to Generate Chemical Hydrogen Storage Materials with Minimal Substituent Weight

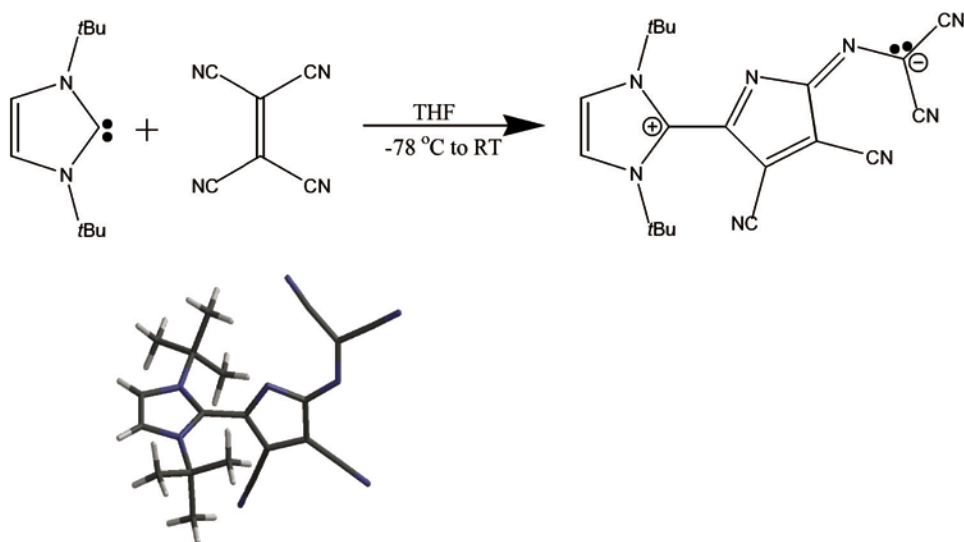


FIGURE 2. Carbene/TCNE Condensation Process and Crystal Structure of the Product

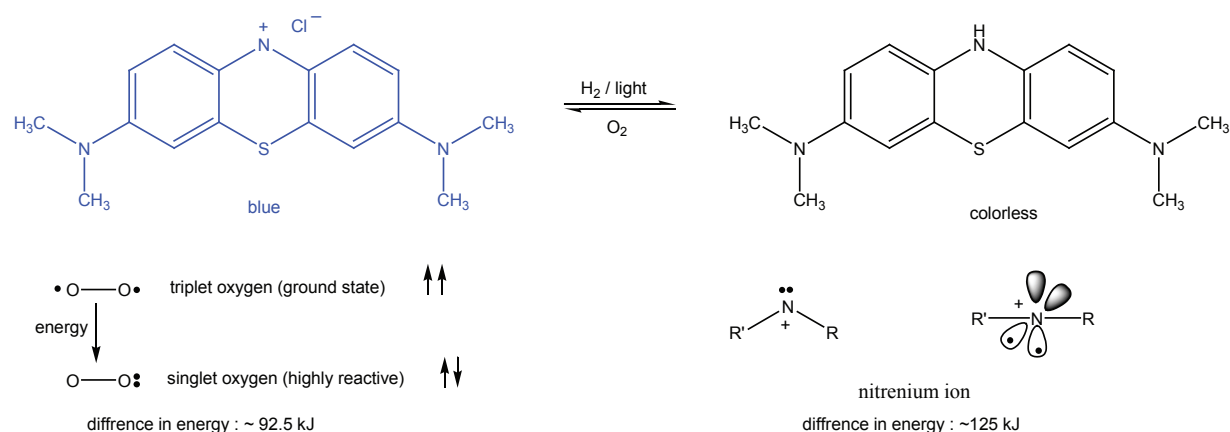


FIGURE 3. Non-Metal Catalyst for H_2 Fixation and Release that is Photoactivated

transferred from the reduced dye to a hydrogen storage substrate to release heat (corresponding to the original light energy absorbed by the dye) and liberate the original dye molecule in its ground state to re-enter the catalytic cycle.

Computational advances include: (1) first set of accurate thermodynamics for $\text{B}_x\text{N}_x\text{H}_y$ compounds up to $x = 3$ and $y = 14$ for release and regeneration of AB in the gas and condensed phases (Table 1). This work includes rings and chains which are critical intermediates in the release of hydrogen; (2) accurate bond energies for AB and related isoelectronic systems which show the strength of the B-N σ -bond in BH_2NH_2 and its importance in driving the overall energetics; (3) studies of the mechanism for H_2 release from AB which identify the potential role of BH_3 as a Lewis acid catalyst (Figure 4) as well as the role of strong Brønsted and Lewis acids in a cationic chain polymerization mechanism for release of H_2 ; (4) predicted the first reliable thermodynamic properties of $\text{B}_3\text{H}_7\text{NH}_3$ and its decomposition mechanism as well as studies of the mechanism of H_2 release from AB dimer $(\text{BH}_3\text{NH}_3)_2$ and from its zwitterionic isomer $[\text{NH}_3\text{BH}_2\text{NH}_3^+][\text{BH}_4^-]$ which show the importance of seeding; (5) continue our reliable, extensive predictions of the energetics for a wide range of regeneration reactions; and (6) continue our extensive studies of carbene, cyanocarbon, and heteroatom diradical chemistry including prediction of the energetics of phosphorus substituted diradicals.

TABLE 1. Thermodynamic Properties of BN Compounds in Different Phases at 298 K from CCSD(T)/CBS (complete basis set) Calculations and Experiment

Compound	Phase	ΔH_f° 298 K kcal/mol	S° 298 K cal/mol·K	Source
BH_3NH_3	gas	-13.5 ± 1.0	57.1	Calc
	solid	-36.6 ± 2.4	23.0	Expt
$\text{B}_3\text{N}_3\text{H}_{12}$	gas	-96.6 ± 1.0	79.3	Calc
	solid	-120.5 ± 4	21.0	ΔH_f° from calc ΔH_f° gas + expt ΔH_{sub} S° from expt
$\text{B}_3\text{N}_3\text{H}_6$	gas	-121.9 ± 3		Expt
	liquid	-129.0 ± 3	47.7	Expt
$\text{B}_3\text{N}_3\text{H}_4$	gas	-115.5 ± 1.0	68.7	Calc
	liquid	-122.6 ± 1.1		Calc + Expt
	solid	-123.6 ± 1.6		Calc + Expt

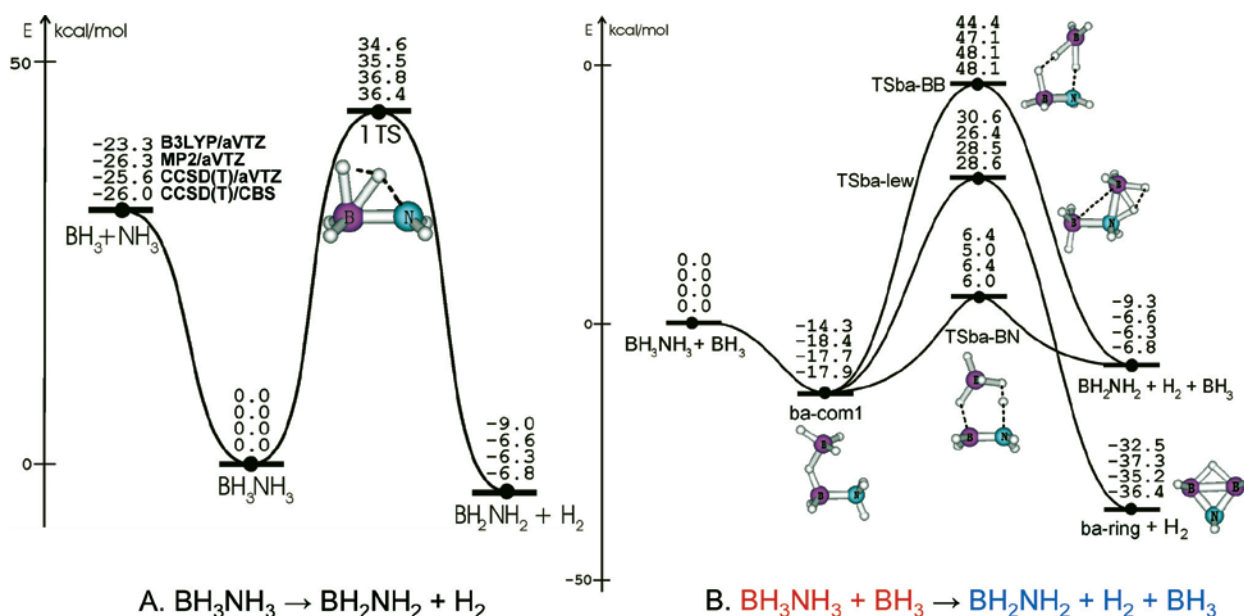


FIGURE 4. Calculated reaction pathways for H_2 release from BH_3NH_3 . Energies in kcal/mol. (A) Reaction path for $\text{BH}_3\text{NH}_3 \rightarrow \text{BH}_2\text{NH}_2 + \text{H}_2$. B-N bond cleavage is energetically more favored over the unimolecular H_2 release from AB. (B) Different reaction paths for $\text{BH}_3\text{NH}_3 + \text{BH}_3 \rightarrow \text{BH}_2\text{NH}_2 + \text{H}_2 + \text{BH}_3$. BH_3 generated by breaking the B-N bond in AB can serve as a Lewis acid catalyst for H_2 elimination from BH_3NH_3 .

Conclusions and Future Directions

We have made substantial progress in the development of new chemistries and computational approaches to meet DOE needs for chemical hydrogen storage. We have developed new models for improving weight percent beyond 1:1 stoichiometry to enable us to meet DOE 2015 goals; shown convergence in the carbene and cyanocarbon approaches; designed a new photoactivated catalyst for H_2 fixation; developed computational thermodynamic and kinetic approaches to meet temperature and pressure requirements as well as stability requirements; used these computational approaches to design new storage systems and design new regeneration mechanisms; and discovered new mechanism for H_2 release and the potential role of Lewis acid catalysts.

Our experimental chemistry goals include:

- Synthesize extended carbene polymers (10.3 wt%, oligomer of TCNE [$\text{C}_2\text{N}_2\text{H}_6$]).
- Synthesis: lower substituent wt% for carbenes.
- Non-metal catalyst for H_2 release for carbenes and TCNE. We are presently scouting other dyes like methyl violet and methyl blue to see what classes of dyes will exhibit this chemistry and which ones can function as hydrogen transfer agents to some ultimate hydrogen storage medium.
- Synthesize extended oligocarbene polymers from carbene chemistry.
- Continue catalyst design and development for H_2 release for carbenes.

Our computational chemistry goals include:

- Continue to support overall CHSCoE efforts in H_2 release, AB regeneration, and new concepts including alternative inorganic and organic compounds and mechanisms. We will use density functional theory benchmarked by accurate molecular orbital theory methods to calculate thermodynamics and kinetics and to develop reaction mechanisms.
- Study the hydrogenation of TCNE. Which sites are hydrogenated in what order? How does hydrogenation of the polycarbene occur?
- Model release of H_2 from silanes for modeling nanocluster chemistry for regeneration.
- Computational design of new catalysts including acid/base catalysts (Lewis acidities, hydride affinities, proton affinities) and transition metals for release and regeneration.
- For B-H regeneration, predict energetics and kinetics of key steps (examples: digestion, reduction, etc.) to optimize experimental approach.
- Predict spectroscopic properties for use in analyzing experimental data.
- Develop improved reaction mechanisms based on predictions of reaction kinetics to optimize processes.
- Study ammonia borane/ammonia trisborane reactions – AB polymers from anionic polymerization.

Special Recognitions & Awards/Patents Issued

1. D.A. Dixon presented the 20th Annual Charles A. Coulson Lecture at the University of Georgia, April, 27, 2007.

FY 2007 Publications/Presentations

1. "The lowest energy states of the Group IIIA – Group VA heteronuclear diatomics: BN, BP, AlN, and AlP from Full Configuration Interaction Calculations," Z. Gan, D. J. Grant, R. J. Harrison, and D. A. Dixon, *J. Chem. Phys.* **2006**, *125*, 124311 (6 pages).
2. "The Heats of Formation of Diazene, Hydrazine, $N_2H_3^+$, $N_2H_5^+$, N_2H , and N_2H_3 and the Methyl Derivatives, CH_3NNH , CH_3NNCH_3 , and $CH_3HNNHCH_3$," M. H. Matus, A. J. Arduengo, III, and D. A. Dixon, *J. Phys. Chem. A*, **2006**, *110*, 10116.
3. "Oxidation of 2,4-Diphosphacyclobutane-1,4-diyl with Ammoniumyl Antimonate and EPR Study of the Corresponding Cation Radical," M. Kikuchi, M. Yoshifuji, A.J. Arduengo, III, T. A. Konovalova, L. Kispert, and S. Ito, *Chem. Lett.* **2006**, *35*(10), 1136.
4. "Acid Initiation of Ammonia-Borane Dehydrogenation for Hydrogen Storage" F. H. Stephens, R. T. Baker, M. H. Matus, D. J. Grant, and D. A. Dixon, *Angew Chem. Int. Ed.*, **2007**, *46*, 746 (Cover and VIP article).
5. "σ- and π-Bond strengths in Main Group 3-5 Compounds," D. Grant and D. A. Dixon, *J. Phys. Chem. A*, **2006**, *110*, 12955.
6. "Theoretical Prediction of the Heats of Formation of C_2H_5O Radicals Derived from Ethanol and of the Kinetics of β-C–C Scission in the Ethoxy Radical," M. H. Matus, M. T. Nguyen, and D. A. Dixon, *J. Phys. Chem. A*, **2007**, *111*, 113.
7. "The Molecular Mechanism for H_2 Release from Amine Borane, BH_3NH_3 , Including the Catalytic Role of the Lewis Acid BH_3 ," M. T. Nguyen, V. S. Nguyen, M. H. Matus, G. Gopakumar, D. A. Dixon, *J. Phys. Chem. A*, **2007**, *111*, 679.
8. "Heats of Formation of Diphosphine, Phosphinophosphinidene, Diphosphine and their Methyl Derivatives, and Mechanism of the Borane-Assisted Hydrogen Release," Myrna H. Matus, Minh Tho Nguyen, and David A. Dixon, *J. Phys. Chem. A*, **2007**, *111*, 1726.
9. "Reliable Predictions of the Thermochemistry of Boron-Nitrogen Hydrogen Storage Compounds: $B_xN_xH_y$, $x = 2, 3$," M. H. Matus, K. D. Anderson, D. M. Camaioni, S. T. Autrey, and D. A. Dixon, *J. Phys. Chem. A*, **2007**, *111*, 4411.
10. "Ammonia Triborane: Theoretical Study of the Mechanism of Hydrogen Release," V. S. Nguyen, M. H. Matus, M. T. Nguyen, and D. A. Dixon, *J. Phys. Chem. A*, WEB ASAP, June, 2007.
11. "Computational Study of the Release of H_2 from Ammonia Borane Dimer $(BH_3NH_3)_2$ and Its Ion Pair Isomers," V. S. Nguyen, M. H. Matus, D. J. Grant, M. T. Nguyen, and D. A. Dixon, *J. Phys. Chem. A*, accepted for publication, June 2007.
12. D.A. Dixon, Invited Lecture, *High level computational approaches to the prediction of the thermodynamics of chemical hydrogen storage systems*, Theory Focus Session on Hydrogen Storage Materials, U.S. DOE H2 Review Meeting, Crystal City, VA, May 2006.
13. A. J. Arduengo, *Novel Architectures Involving Imidazol-2-ylidenes: Structure and Chemistry*, Chemistry Department, University of Zurich, Switzerland, November 2007.
14. A. J. Arduengo, *Novel Architectures Involving Imidazol-2-ylidenes: Structure and Chemistry*, Chemistry Department, University of Bonn, Germany, November 2007.
15. A. J. Arduengo, *Novel Architectures Involving Imidazol-2-ylidenes: Structure and Chemistry*, Chemistry Department, Technical University of Braunschweig, Germany, December 2007.
16. D.A. Dixon, Invited Lecture, *Recent Advances in Computational Inorganic Chemistry*, Loker Hydrocarbon Research Institute and Department of Chemistry Symposium Honoring Professor Karl O. Christe on the Occasion of his 70th Birthday, University of Southern California, Los Angeles, CA, January 2007.
17. D.A. Dixon, Invited Lecture, *Recent Advances in Computational Inorganic Chemistry*, Chemical Engineering Department, Mississippi State, Starksville, MS, January 2007.
18. D.A. Dixon, Invited Lecture: *Recent Advances in Computational Inorganic Chemistry*, Physical Chemistry Division, Chemistry Department, University of Maryland, College Park, MD, February 2007.
19. D.A. Dixon, Invited Lecture: *Recent Advances in Computational Inorganic Chemistry*, Inorganic Division, Chemistry Department, Florida State University, Tallahassee, FL, March 2007.
20. D.A. Dixon, *Recent Advances in Computational Inorganic Chemistry*, 20th Annual Charles A. Coulson Lecture at the University of Georgia, April, 27, 2007, Athens, GA.
21. Myrna H. Matus, Kevin D. Anderson, and David A. Dixon, Donald M. Camaioni and S. Thomas Autrey, Poster, *Computational Studies on Boron-Nitrogen Compounds and Methylated Derivatives For Chemical Hydrogen Storage*, 36th Annual Conference of the Southeast Theoretical Chemists' Association, May 18 and 19, 2007, Virginia Tech, Blacksburg, VA.
22. Minh Tho Nguyen, Myrna H. Matus, Vinh Son Nguyen, and David A. Dixon, Talk, *Molecular Mechanism of Hydrogen Release Reactions from Boron-Nitrogen Compounds*, 36th Annual Conference of the Southeast Theoretical Chemists' Association, May 18 and 19, 2007, Virginia Tech, Blacksburg, VA.